

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number
WO 2004/005437 A1

(51) International Patent Classification⁷: **C10G 70/06, 70/04**

[NL/NL]; Zomergemstraat 40, NL-4826 CW Breda (NL).
LEUNK, Hendrek, Derk [NL/NL]; Vrijheidslaan 12, NL-4533 AA Terneuzen (NL).

(21) International Application Number:

PCT/NL2003/000474

(74) Agent: **SCHMEETZ, M., M., H., J.**; DSM Intellectual Property, P.O. Box 9, NL-6160 MA Geleen (NL).

(22) International Filing Date: 27 June 2003 (27.06.2003)

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02077666.2 5 July 2002 (05.07.2002) EP

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

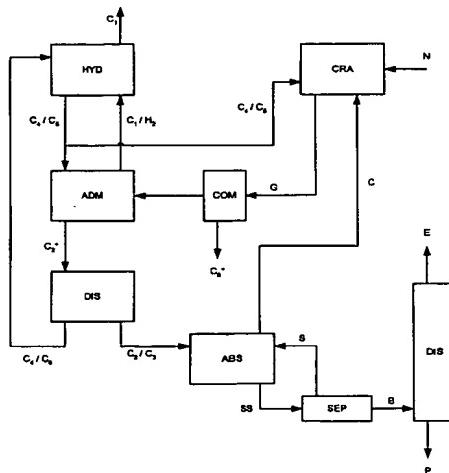
(71) Applicant (for all designated States except US): **SABIC HYDROCARBONS BV** [NL/NL]; Poststraat 1, NL-6135 KR Sittard (NL).

Published:

— with international search report

[Continued on next page]

(54) Title: PROCESS FOR THE RECOVERY OF AN ETHYLENE AND PROPYLENE CONTAINING STREAM FROM A CRACKED GAS RESULTING FROM HYDROCARBON CRACKING



(57) Abstract: Process for the recovery of an ethylene and propylene containing stream from a cracked gas resulting from cracking a hydrocarbon stream, wherein the cracked gas is treated in an absorptive demethanizer with a C₄/C₅ solvent at a temperature between -10 °C and -40 °C to free the cracked gas from methane and hydrogen gas, whereafter the remaining stream is treated by distillation in a distillation unit to obtain a C₄/C₅ containing stream and the ethylene and propylene containing stream; whereafter the C₄/C₅ stream is treated with a hydrogen containing stream in a hydrogenation unit, whereafter a part of the hydrogenated C₄/C₅ stream is cooled to a temperature between -10 °C and -40°C and recycled to the absorptive demethanizer and a part of the hydrogenated C₄/C₅ stream is separated.

W 2004/005437 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

5 PROCESS FOR THE RECOVERY OF AN ETHYLENE AND PROPYLENE
CONTAINING STREAM FROM A CRACKED GAS RESULTING FROM
HYDROCARBON CRACKING

10 The invention relates to a process for the recovery of an ethylene and propylene containing stream from a cracked gas resulting from cracking a hydrocarbon stream.

15 The hydrocarbon cracking to obtain ethylene and propylene is disclosed in for example Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 10, 1996, p. 45-93. Besides the ethylene and the propylene also other products for example cracked fuel oil, hydrogen, methane, C₄-material and pyrolysis gasoline result from the hydrocarbon cracking. Some of these products have commercial value but actually a lot of these products are only undesired coproducts. Generally, the recovery of ethylene and propylene with a good yield is the main aim for hydrocarbon cracking.

20 It is the object of the present invention to recover an ethylene and propylene containing stream from a hydrocarbon cracker whereas the undesired coproducts are not obtained in the recovery section as separate products.

25 The invention is characterized in that the cracked gas is treated in an absorptive demethanizer with a C₄/C₅ solvent at a temperature between -10 °C and -40 °C to free the cracked gas from methane and hydrogen gas, whereafter the remaining stream is treated in a distillation unit to obtain a C₄/C₅ containing stream and the ethylene and propylene containing stream; whereafter the C₄/C₅ stream is treated with a hydrogen containing stream in a hydrogenation unit, whereafter a part of the hydrogenated C₄/C₅ stream is cooled to a temperature between -10 °C and -40 °C and recycled to the absorptive demethanizer and a part of the hydrogenated C₄/C₅ stream is separated and may, for instance, be recycled to the hydrocarbon cracker.

30 Hydrogen, C₄ and C₅ material are used within the process according to the invention and consequently they are not recovered as separate products.

Another advantage of the present process is the improved yield of ethylene and propylene.

35 Preferably, the propylene/ethylene ratio (P/E ratio) is higher than 0.55.

In the process according to the invention an absorptive demethanizer is used and as a result thereof no deep cooling is necessary and no expensive material is necessary for the demethanizer column.

The cracked gas resulting from hydrocarbon cracking is obtained by 5 cooling and compressing the gas resulting from cracking. In the compression section the cracked gas is compressed in several stages and the hydrocarbons containing 6 or more carbon atoms (C_6^+) are removed from the cracked gas. Acid gases may, for instance, be removed in a caustic wash tower and the heavy ends may be removed from the cracked gas by distillation. It is also possible to hydrogenate the cracked gas 10 in a front-end hydrogenation unit before introduction in the absorptive demethanizer to remove acetylenes and propadiene from the cracked gas.

The hydrogenation is performed by contacting the cracked gas with a 15 hydrogenation catalyst. Hydrogenation is performed at a pressure between 1.5 and 5.0 MPa and a temperature between 25 °C and 100 °C. Generally, a hydrogenation catalyst contains a metal compound comprising Ni, Pd, Pt and/or Co.

Preferably, the catalyst is a Pd-containing catalyst.

Preferably, the hydrogenation catalyst is a supported catalyst.

Examples of suitable carrier materials are silica, α -, θ - and γ -alumina, zeolites, carbon 20 and oxidic carriers, such as for instance magnesium oxide, titanium oxide and/or zirconium oxide. By preference, the carrier material is θ - and γ -alumina, silica or carbon. Most preferably θ - or γ -alumina are used as carrier material because this is an inert carrier material with a large total surface area and a good poor volume distribution. Generally, the metal content of the catalyst ranges between 10 and 25 wt%. Supported catalysts are commercially available with for instance 10, 15 and 20 25 wt% of metal.

Additionally the catalyst may also contain minor amounts of compounds which enhance the activity and selectivity of the catalyst. Examples of such compounds include: chromium, gold, rhodium and/or ruthenium. The catalyst may also be modified with a sulphur-containing compound.

30 The C_4/C_5 solvent is present within the loop comprising the absorptive demethanizer, a distillation unit and a hydrogenation unit. The C_4/C_5 stream comprises all compounds with 4 or 5 carbon atoms out of the cracked gas. An amount less than 15 wt% of hydrocarbon compounds with 6 or more carbon atoms is allowed to be present in the C_4/C_5 stream.

35 The cracked gas is first treated in an absorptive demethanizer to free

the cracked gas from methane and hydrogen by using a C₄/C₅ solvent and a cooling medium simultaneously. It dissolves the hydrocarbons out of the cracked gas, except the hydrogen gas and methane, which are removed from the absorptive demethanizer. The temperature in the absorptive demethanizer is between -10 °C and -40 °C and the 5 pressure is between 0.1 and 5.0 MPa.

The remaining stream, being the C₄/C₅ stream combined with the hydrocarbons having 2-5 carbon atoms out of the cracked gas, is treated by distillation at a pressure between 0.5 and 2.0 MPa and at a temperature between -40 °C and 150 °C. An ethylene and propylene containing stream is obtained and the C₄/C₅ stream is 10 thereafter fed to a hydrogenation unit where it is substantially or partly hydrogenated. A part of the C₄/C₅ stream is separated from the loop after hydrogenation. The remaining stream is cooled and recycled as a solvent to the absorptive demethanizer.

It is possible to apply more than one hydrogenation unit. The 15 hydrogenation may be performed with hydrogen gas from the absorptive demethanizer or with hydrogen gas from another source. Preferably, the hydrogen gas resulting from the absorptive demethanizer is used for the hydrogenation. This hydrogen gas may be used as a hydrogen mixture with methane as it is resulting from the absorptive demethanizer or it can first be separated from the methane gas.

The reactor for the hydrogenation may be a packed-bed or a trickle- 20 bed reactor. The flow within the reactor is a cocurrent or a countercurrent flow. The hydrogenation temperature generally ranges between 25 °C and 100 °C.

The C₄/C₅ stream may be substantially or partly hydrogenated to remove the unsaturated compounds. In case the C₄/C₅ stream is substantially 25 hydrogenated the C₄/C₅ stream comprises at most 15 wt% of unsaturated compounds. In case the C₄/C₅ stream is partly hydrogenated the amount of unsaturated compounds in the C₄/C₅ stream is between 50 and 90 wt% and preferably between 70 and 90 wt%.

When the C₄/C₅ stream is substantially hydrogenated a part of it is separated from the loop and may, for instance, be recycled to the hydrocarbon cracker.

When the C₄/C₅ stream is partly hydrogenated a part of it is 30 separated from the loop, it is preferably treated by catalytic cracking. The aim of catalytic cracking is to recover ethylene and propylene out of the unsaturated C₄/C₅ stream. By the catalytic cracking of the C₄/C₅ stream not only the yield of ethylene and propylene obtained with the process according to the invention is higher, but also the propylene/ethylene ratio (P/E ratio) is improved. By the catalytic cracking of the 35 unsaturated C₄/C₅ stream a P/E ratio higher than 0.70, preferably higher than 0.75,

may be obtained.

The catalytic cracking may be performed in one or more reactors. The temperature during catalytic cracking is between 400 °C and 800 °C and the pressure is between 0.05 and 0.5 MPa. All known processes for catalytic cracking can
5 be used.

The ethylene and propylene containing stream obtained after distillation of the C₄/C₅ stream combined with the hydrocarbons with 2-5 carbon atoms out of the cracked gas is led to a chemical absorption unit. In the chemical absorption unit ethylene and propylene are chemically absorbed from the ethylene and propylene
10 containing stream, in a solvent containing a compound derived from a metal of group 10 or 11 of the Periodic Table of the Elements, followed by recovery of ethylene and propylene from said solvent by heating and/or by reducing the pressure. The ethylene and propylene-containing stream is substantially free of hydrogen, acetylenes and dienes.

15 The Periodic Table of the Elements is disclosed on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990.

The ethylene and propylene containing stream mainly comprises ethylene, ethane, propylene and propane. Ethylene and propylene are separated from ethane and propane by subjecting the ethylene and propylene containing stream to a
20 chemical absorption process. The chemical absorption process is performed by contacting the ethylene and propylene containing stream and a solvent containing a compound derived from a metal of group 10 or 11 of the Periodic Table of the Elements.

25 Preferably, the metal compound comprises Cu or Ag. Examples of suitable Ag-containing compounds are silver acetate, silver nitrate and/or silver tetrafluoroborate. Examples of suitable Cu-containing compounds are cuprous nitrate, cuprous sulphate, cuprous tetrafluoroborate, cuprous tetrachloroaluminate and/or cuprous diketonate.

Suitable solvents used in the chemical absorption process are water
30 or aromatic and olefinic solvents. Examples of aromatic and olefinic solvents are alfa-methylstyrene, benzene and toluene. Generally, Ag-containing compounds are used in combination with water as the solvent whereas Cu-containing compounds may be used with water as the solvent and also in the presence of a stabilizer such as, for instance ammonia, pyridine or an alkanolamine. Cu-containing compounds are usually dissolved
35 in aromatic or olefinic solvents.

Most preferably, the solvent is water and the metal compound is AgNO_3 . The concentration of the compound in the solvent may be between 2 and 15 mol/l.

The ethylene and propylene containing stream is contacted with the 5 solvent for chemical absorption at a temperature between 0 °C and 50 °C and a pressure of 0.5 to 3.0 MPa.

Ethane and propane may be recycled to the hydrocarbon cracker.

Ethylene and propylene which are absorbed are recovered from the solvent by heating and/or by reducing the pressure. It is also possible to heat the 10 solvent first, where after the pressure is reduced or vice versa.

Preferably, the temperature and the pressure at which ethylene and propylene are released from the solvent is between 80 °C and 150 °C and between 0.1 and 1.0 MPa. Thereafter this product stream is separated in an ethylene stream and a propylene stream by distillation at a pressure between 0.1 and 3.0 MPa and a 15 temperature between –60 °C and 100 °C.

The invention is also directed to a recovery section of a hydrocarbon cracker and the invention is also directed to a method to modify an existing hydrocarbon cracker by providing it with a recovery section according to the invention.

The invention will be further explained with respect to Figure 1 and 20 Figure 2 without being limited thereto.

Example I

Figure 1 shows the recovery section of a hydrocarbon cracker. A naphtha feedstock (N) (1000 t/h) was cracked in a hydrocarbon cracker (CRA). In the 25 compression section (COM) the cracked gas was compressed in several stages and the hydrocarbons containing 6 or more carbon atoms (C_6^+) were removed from the cracked gas.

The cracked gas was thereafter led to an absorptive demethanizer (ADM) where it was treated with a C_4/C_5 solvent (C_4/C_5) at a temperature of –30°C. The 30 composition of the C_4/C_5 solvent was 50 wt% n-butane, 15 wt% i-butane, 10 wt% n-pentane, 5 wt% i-pentane, 10 wt% cyclopentane, 2 wt% other C_4 and C_5 compounds and 8 wt% C_6 compounds.

In the ADM hydrogen gas and methane (C_1/H_2) were separated from the cracked gas and the resulting stream (C_2^+) was led to a distillation unit (DIS) where 35 the stream was treated at 0.1 MPa; top temperature –19 °C and bottom temperature 86

°C; in an ethylene and propylene containing stream (C_2/C_3) and a C_4/C_5 stream (C_4/C_5).

The C_2^+ stream comprised 23 wt% ethylene, 13 wt% propylene, 27 wt% n-butane, 8 wt% i-butane, 6 wt% n-pentane, 3 wt% l-pentane, 6 wt% cyclopentane and 12 wt% other compounds.

5 The C_2/C_3 stream comprised 2 wt% methane, 9 wt% ethane, 57 wt% ethylene, 1 wt% propane and 31 wt% propylene.

 The C_4/C_5 stream comprised 45 wt% n-butane, 14 wt% i-butane, 11 wt% n-pentane, 4 wt% l-pentane, 9 wt% cyclopentane, 8 wt% other C_4 compounds and 9 wt% other C_5 compounds.

10 This C_4/C_5 stream was led to a hydrogenation unit. Hydrogenation is performed with C_1/H_2 coming from the ADM. After hydrogenation C_1 was separated about 20 wt% of C_4/C_5 was separated and recycled to the CRA. The other part of C_4 was cooled to -35 °C and introduced in the ADM.

15 The C_2/C_3 stream was led to a chemical absorption unit (ABS) and was contacted in this unit with a solvent (S) containing $AgNO_3$ at a temperature of 25 °C and a pressure of 1.0 MPa. The concentration of the $AgNO_3$ in the solvent was 6 mol/l. The solvent was water. Ethylene and propylene were absorbed in the solvent and ethane and propane (C) were removed from ABS. C was recycled to a hydrocarbon cracker. The solvent containing ethylene and propylene (SS) was led to a separation unit wherein the pressure was released to 0.6 MPa. Thereafter the temperature in the separation unit was raised to 100 °C to remove ethylene and propylene from it whereafter S was recycled to ABS. The combined ethylene and propylene stream (B) was led to a distillation unit to separate B in ethylene (E) and propylene (P). The pressure during distillation was 1.8 MPa. The top temperature was 25 -32 °C and the bottom temperature was 44 °C.

 An amount of 387 t/h of E with a purity of 99.999 wt% was obtained and an amount of 215 t/h of P with a purity of 99.98 wt% was obtained.

Example II

30 In figure 2 the recovery section is the same as the recovery section according to figure 1. The cracking process and recovery process that was performed was based on the same cracked gas as the process according to Example I.

 Naphtha was fed to the hydrocarbon cracker with 1000 t/h.

 In figure 2 the hydrogenation unit (HYD) is so designed that not all 35 unsaturated compounds in C_4/C_5 are hydrogenated and the part of C_4/C_5 that is

separated is treated by catalytic cracking with a zeolite catalyst at a temperature of 560 °C and a pressure of 0.15 MPa. After catalytic cracking the C₄/C₅ stream was separated in 2 different streams by distillation. An extra ethylene and propylene containing stream was obtained which was, together with the C₂/C₃ stream resulting

5 from DIS introduced in ABS.

Further a C₄⁺ stream, containing a lot of aromatics, was obtained that was separated together with the C₆⁺ stream and a stream containing hydrocarbons with 1 to 3 carbon atoms comprising some hydrogen. This stream (C₃) was recycled to COM.

10 An amount of 359 t/h of E with a purity of 99.999 wt% and an amount of 274 t/h of P with a purity of 99.98 wt% was obtained.

CLAIMS

1. A process for the recovery of an ethylene and propylene containing stream from a cracked gas resulting from cracking a hydrocarbon stream,
5 characterised in that the cracked gas is treated in an absorptive demethanizer with a C₄/C₅ solvent at a temperature between –10 °C and –40 °C to free the cracked gas from methane and hydrogen gas, whereafter the remaining stream is treated by distillation in a distillation unit to obtain a C₄/C₅ containing stream and the ethylene and propylene containing stream; whereafter the
10 C₄/C₅ stream is treated with a hydrogen containing stream in a hydrogenation unit, whereafter a part of the hydrogenated C₄/C₅ stream is cooled to a temperature between –10 °C and –40 °C and recycled to the absorptive demethanizer and a part of the hydrogenated C₄/C₅ stream is separated.
2. A process according to Claim 1 characterised in that the C₄/C₅ stream is
15 hydrogenated with the use of the hydrogen gas coming from the absorptive demethanizer.
3. A process according to any one of Claims 1-2, characterised in that the C₄/C₅ stream is substantially hydrogenated in the hydrogenation unit.
4. A process according to any one of Claims 1-3, characterised in that the C₄/C₅
20 stream is partly hydrogenated in the hydrogenation unit and part of the C₄/C₅ stream is separated after the hydrogenation unit and treated by catalytic cracking, whereafter an additional ethylene and propylene containing stream is obtained.
5. A process according to any one of Claims 1-4, characterised in that from the
25 ethylene and propylene containing stream, being substantially free of hydrogen, acetylenes and dienes, ethylene and propylene are chemically absorbed in a solvent containing a compound derived from a metal of group 10 or 11 of the Periodic Table of the Elements, followed by recovery of ethylene and propylene from said solvent by heating and/or by reducing the pressure.
6. A process according to any one of Claims 1-5, characterised in that the
30 propylene/ethylene ratio in the ethylene and propylene containing stream is higher than 0.55.
7. A process according to Claim 4, characterised in that the propylene/ethylene ratio in the combined ethylene and propylene containing stream is higher than
35

0.70.

8. A recovery section of a hydrocarbon cracker comprising an absorptive demethanizer, a distillation unit and a hydrogenation unit wherein a process according to any one of Claims 1-2 is applied.
- 5 9. A recovery section according to Claim 8, characterised in that the hydrogenation in the hydrogenation unit takes place with hydrogen gas from the absorptive demethanizer.
10. A method to modify an existing hydrocarbon cracker by providing it with a recovery section according to any one of Claims 8-9.

10

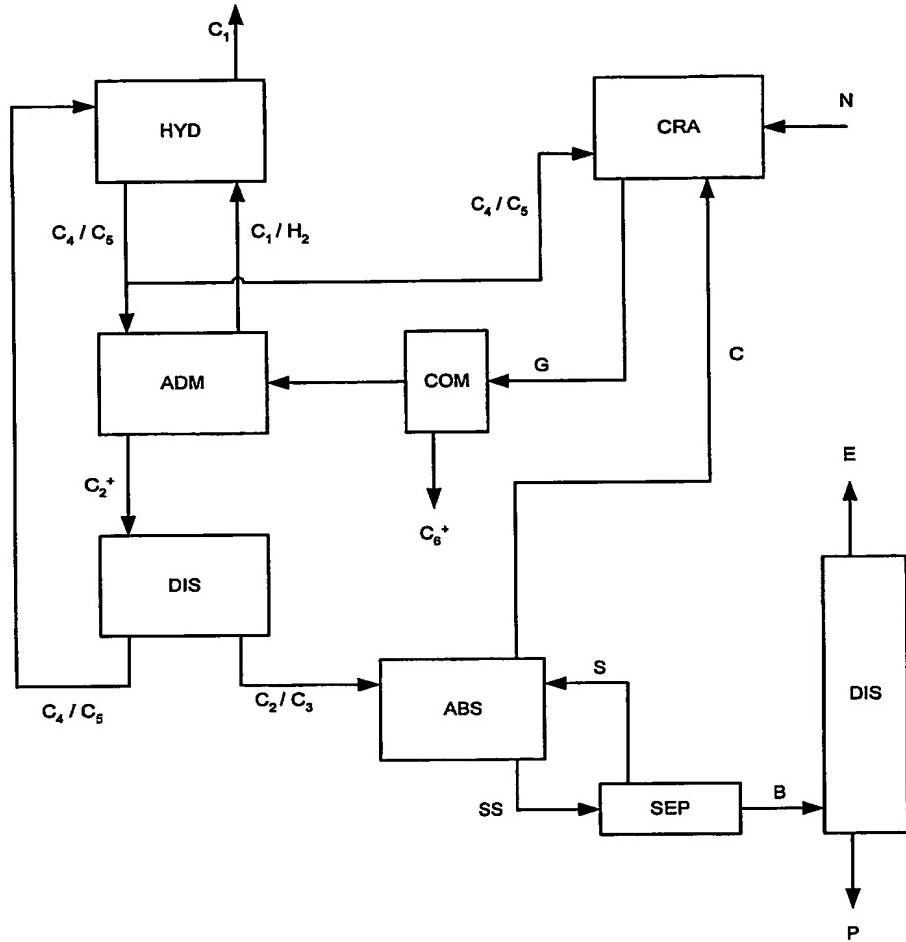


Figure 1

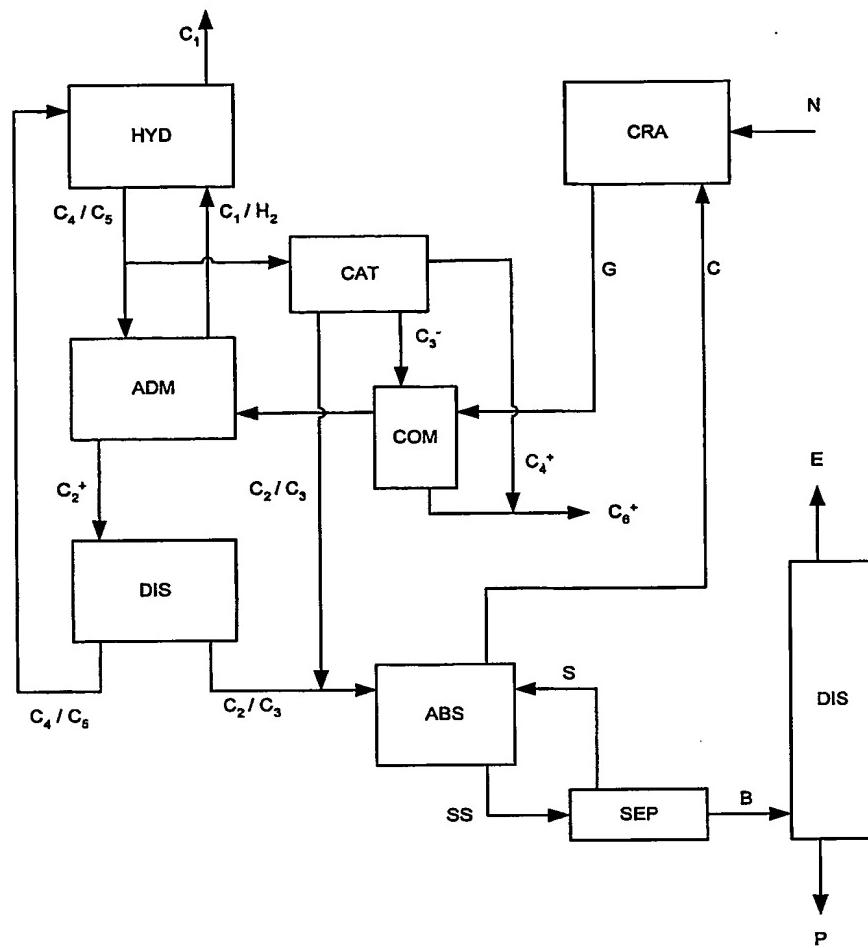


Figure 2

INTERNATIONAL SEARCH REPORT

PCT/NL 03/00474

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C10G70/06 C10G70/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 520 724 A (BAUER HEINZ ET AL) 28 May 1996 (1996-05-28) column 2, line 26 - line 28; figure 1 column 3, line 26 - column 5, line 10 ---	1,3,8,10
Y	FR 2 797 640 A (INST FRANCAIS DU PETROL) 23 February 2001 (2001-02-23) page 3, line 10 -page 4, line 9; figure 1 page 12, line 1 - line 4 ---	1,3,8,10
A	US 5 859 304 A (BARCHAS RICHARD ET AL) 12 January 1999 (1999-01-12) column 10, line 9 - line 65; figures column 11, line 36 - line 38 ---	1-7
A	US 5 551 972 A (WOOD GLENN C ET AL) 3 September 1996 (1996-09-03) abstract; figure 3 ---	1-10 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the International search

Date of mailing of the International search report

24 October 2003

31/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bertin-van Bommel, S

INTERNATIONAL SEARCH REPORT

PCT/NL 03/00474

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 326 929 A (MEHRA YUV R ET AL) 5 July 1994 (1994-07-05) abstract; claims; figures -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 03/00474

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 5520724	A	28-05-1996	DE AT AU AU CA DE WO EP ES JP MX NO ZA	4217611 A1 125241 T 671277 B2 4067293 A 2136629 A1 59300380 D1 9324428 A1 0625134 A1 2074927 T3 8506082 T 9303089 A1 944521 A 9303662 A		02-12-1993 15-08-1995 22-08-1996 30-12-1993 09-12-1993 24-08-1995 09-12-1993 23-11-1994 16-09-1995 02-07-1996 30-06-1994 25-11-1994 21-12-1993
FR 2797640	A	23-02-2001	FR US	2797640 A1 6340429 B1		23-02-2001 22-01-2002
US 5859304	A	12-01-1999	AU AU CN EP HU JP KR NO WO	729214 B2 5692898 A 1239938 A ,B 0951463 A1 9904163 A2 2001507682 T 2000057553 A 992855 A 9825871 A1		25-01-2001 03-07-1998 29-12-1999 27-10-1999 28-04-2000 12-06-2001 25-09-2000 11-08-1999 18-06-1998
US 5551972	A	03-09-1996	US AU WO	5462583 A 1981895 A 9523835 A1		31-10-1995 18-09-1995 08-09-1995
US 5326929	A	05-07-1994	US AU AU BR CA CN DE DE EP JP JP KR RU WO	5220097 A 671086 B2 2795792 A 9207086 A 2130567 A1 1075707 A ,B 69219365 D1 69219365 T2 0626989 A1 7507078 T 3242109 B2 230672 B1 2105036 C1 9317081 A1		15-06-1993 15-08-1996 13-09-1993 12-12-1995 02-09-1993 01-09-1993 28-05-1997 07-08-1997 07-12-1994 03-08-1995 25-12-2001 15-11-1999 20-02-1998 02-09-1993